

1 PLASMA ENHANCED ALD OF TANTALUM NITRIDE AND BILAYER

2
3 FIELD OF THE INVENTION
4

5 This invention relates to electrical interconnection
6 structures. More particularly, it relates to "back end
7 of the line" (BEOL) interconnections in high
8 performance integrated circuits, and diffusion barriers
9 used in such devices.

10
11 BACKGROUND OF THE INVENTION
12

13 In view of the fact that copper has higher
14 electromigration resistance, and thus reliability, as
15 well as higher conductivity than aluminum wiring,
16 copper interconnects are being widely accepted as
17 standard interconnect technology in semiconductor
18 device fabrication. However, for successful
19 implementation of copper interconnect technology,
20 proper diffusion barrier materials with high thermal
21 stability, low resistivity, and low reactivity with
22 copper are essential since copper has higher
23 diffusivity than aluminum and copper easily diffuses
24 through dielectrics, producing deep level defects which
25 are detrimental to the performance of CMOS transistors.
26 It is for this reason that a thin tantalum/tantalum
27 nitride (Ta/TaN) bilayer is usually used as a diffusion
28 barrier to encapsulate the copper lines and vias used
29 with copper interconnect features. Currently ionized
30 physical vapor deposition (I-PVD) is the conventional
31 deposition technique used for the formation of these
32 Ta/TaN layers. However, the use of PVD technologies

1 for these layers is not expected to be applicable for
2 technologies using nodes smaller than approximately 45
3 nanometers due to limited ability of the deposited
4 films to conform to these smaller features.

5
6 Recently, as an alternative deposition technique,
7 atomic layer deposition (ALD) has been widely studied.
8 Due to the inherent atomic level control and
9 self-saturation chemistry, the films formed by ALD are
10 highly conformal and uniform. While it is possible to
11 deposit metallic Ta films using ALD with a halide
12 tantalum precursor, the ALD of Ta and TaN as a bilayer
13 has been only rarely successful for two reasons.
14 First, the conventionally available ALD of TaN using an
15 inorganic source (such as TaCl_5), reacted with ammonia
16 (NH_3) has been reported to produce a highly resistive
17 phase of tantalum nitride, the Ta_3N_5 phase, which
18 presents practical difficulties for the use of these
19 films as barriers in conducting circuits. Second,
20 while it is possible to deposit TaN films using a
21 metal-organic Ta source such as, for example, TBTDET
22 (tertbutylimidotris(diethylamido)tantalum), it is
23 impossible to use this precursor for the deposition of
24 a metallic Ta film by ALD since the TaN bond cannot be
25 reduced in this chemical system.

26
27 Tantalum plasma enhanced ALD (PE-ALD) using chlorides
28 and atomic hydrogen as the metal precursor and reagent
29 has been developed recently. An excellent explanation
30 of ALD and apparatus for performing ALD may be found in

1 Plasma-Enhanced Atomic Layer Deposition of Ta and Ti
2 For Interconnect Diffusion Barriers by S.M. Rossnagel,
3 J. Vac. Sci. Technol. B18(4), July/Aug. 2000, which is
4 incorporated herein by reference in its entirety.

5
6
7

SUMMARY OF THE INVENTION

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9 It is therefore an aspect of the present invention to
10 provide a method for producing a copper diffusion
11 barrier that is reliable.

12

13 It is another object of the invention to provide a
14 copper diffusion barrier that is made up of materials
15 of relatively high purity, and in particular materials
16 that are carbon free.

17

18 The present invention is directed to a novel and simple
19 method for depositing a tantalum nitride layer with
20 controllable nitrogen content and a tantalum
21 nitride/tantalum barrier using PE-ALD. Low resistivity
22 cubic tantalum nitride thin films may be grown by
23 plasma-enhanced atomic layer deposition (PE-ALD) using
24 a tantalum halide, such as TaCl₅ as the metal precursor
25 and a hydrogen/nitrogen plasma. The deposition can be
26 performed by alternate exposures of TaCl₅ and a plasma
27 composed of a mixture of hydrogen and nitrogen or the
28 consecutive exposure of hydrogen plasma and nitrogen
29 plasma. The nitrogen content in the films can be
30 controlled from a nitrogen to tantalum ratio of 0 up to
31 1.7 by changing nitrogen partial pressure during the

1 second, reactant step of the ALD sequence. A bilayer
2 (or multilayer) of tantalum nitride/tantalum can be
3 deposited by simply switching off the nitrogen flow
4 following the deposition of tantalum nitride. This
5 bilayer shows good copper diffusion barrier properties.

6

7 Thus, the invention is directed to a method for forming
8 a tantalum nitride layer on a substrate comprising
9 depositing the layer on the substrate by plasma
10 enhanced atomic layer deposition of a tantalum halide
11 precursor in the presence of a hydrogen plasma and a
12 nitrogen plasma. Preferably, the tantalum halide
13 precursor is tantalum pentachloride. The method
14 further comprises varying concentration of nitrogen
15 plasma to thereby vary the amount of nitrogen in the
16 layer. The concentration of nitrogen plasma may be
17 varied so that the layer has a nitrogen to tantalum
18 concentration ratio of between 0 and 1.7. The method
19 may further comprise reducing the concentration of
20 nitrogen plasma to zero so that a substantially
21 nitrogen free layer of tantalum is formed. Thus, the
22 concentration of nitrogen is other than zero for a
23 first period of time, and the concentration of nitrogen
24 plasma is essentially zero for a second period of time,
25 so that a first layer of tantalum nitride is formed and
26 a second layer of substantially nitrogen free tantalum
27 is formed. The combination of the first layer and the
28 second layer can be used as a diffusion barrier for
29 copper. Preferably, the second layer is deposited upon
30 the first layer.

1 During deposition, the temperature of the substrate is
2 between 100 °C and 400 °C, and may be 300 °C.

3

4 The layer is deposited on a substrate selected from the
5 group consisting of silicon, silicon having a layer of
6 silicon dioxide on the silicon and other dielectric
7 materials which have low dielectric constants including
8 porous dielectrics. The low dielectric constant
9 substrates may have a dielectric constant in the range
10 of 2.0 to 3.0. The substrate may have copper
11 conductors.

12

13 In accordance with the invention, the deposition may
14 comprise exposing the substrate to the tantalum halide
15 carried by an inert gas; exposing the substrate to the
16 hydrogen and nitrogen plasma; and repeating these
17 steps, for example, for a total of 40 to 250 times,
18 until a desired thickness of the layer of, for example,
19 2 to 10 nanometers is obtained. The exposure of the
20 substrate to the tantalum halide carried by the inert
21 gas may be performed at a pressure of 3.0×10^{-2} Torr.
22 During the exposure of the substrate to the hydrogen
23 and nitrogen plasma, the partial pressure of hydrogen
24 may be 2.5×10^{-2} Torr. The exposure of the substrate
25 to the tantalum halide carried by the inert gas may be
26 carried out for approximately 2 seconds; and exposure
27 of the substrate to the hydrogen and nitrogen plasmas
28 may be carried out for approximately 5 seconds. The
29 substrate may be simultaneously or sequentially exposed
30 to the nitrogen plasma and the hydrogen plasma.

1 The invention is also directed to an article of
2 manufacture comprising a substrate; and a bilayer of
3 tantalum nitride and tantalum on the substrate, each of
4 the tantalum nitride and the tantalum being
5 substantially free of carbon. Preferably, the tantalum
6 layer comprises amorphous tantalum. Also preferably
7 the tantalum is disposed on the tantalum nitride.

8
9 BRIEF DESCRIPTION OF THE DRAWINGS

10
11 These and other aspects, features, and advantages of
12 the present invention will become apparent upon further
13 consideration of the following detailed description of
14 the invention when read in conjunction with the drawing
15 figures, in which:

16
17 Fig. 1 shows a series of graphs of x-ray diffraction
18 data (intensity verses angle) for TaNx layers deposited
19 by PE-ALD at various ratios of partial pressure of
20 nitrogen to partial pressure of hydrogen.

21
22 Fig. 2 is a graph which shows nitrogen content and
23 growth rate of TaNx layers deposited by PE-ALD as a
24 function of the ratio of partial pressure of nitrogen
25 to partial pressure of hydrogen.

26
27 Fig. 3 is a graph of the resistivity of TaNx layers
28 produced by PE-ALD as a function of the N/Ta ratio.

1 Fig. 4 is a graph which shows nitrogen content and
2 growth rate of TaNx layers deposited by PE-ALD as a
3 function of the plasma exposure time at a given ratio
4 of plasma partial pressures and at a given temperature.

5
6 Fig. 5 is a graph which shows chlorine and hydrogen
7 content and resistivity values as a function of the
8 plasma exposure time at a given ratio of plasma partial
9 pressures and at a given temperature.

10
11 Fig. 6 shows a series of graphs of x-ray diffraction
12 data (intensity verses angle) at various growth
13 temperatures.

14
15 Fig. 7 is a graph which shows nitrogen content and
16 growth rate of TaNx layers deposited by PE-ALD as a
17 function of temperature.

18
19 Fig. 8 is a graph which shows chlorine and hydrogen
20 content and resistivity of TaNx layers deposited by
21 PE-ALD as a function of temperature.

22
23 Fig. 9 illustrates copper diffusion barrier failure as
24 a function of annealing temperature for PE-ALD TaN/Ta
25 bilayers.

26
27 DESCRIPTION OF THE INVENTION

28
29 Variations described for the present invention can
30 be realized in any combination desirable for each

1 particular application. Thus particular limitations,
2 and/or embodiment enhancements described herein,
3 which may have particular advantages to the
4 particular application need not be used for all
5 applications. Also, it should be realized that not all
6 limitations need be implemented in methods, systems
7 and/or apparatus including one or more concepts of the
8 present invention.

9
10 An apparatus which may be used to perform the method in
11 accordance with the invention is described in the above
12 mentioned paper entitled Plasma-Enhanced Atomic Layer
13 Deposition of Ta and Ti For Interconnect Diffusion
14 Barriers by S.M. Rossnagel, J. Vac. Sci. Technol.
15 B18(4), July/Aug. 2000. As noted above the teachings
16 of this paper are incorporated herein by reference in
17 their entirety.

18
19 Sample sizes as large as, for example, but not by way
20 of limitation, 200 mm in diameter are loaded into a
21 commercially available or non-commercial ALD chamber.
22 The chamber is pumped by a reactive-gas grade turbo
23 molecular vacuum pump with a working base pressure of
24 10^{-7} Torr. The sample may be heated using a heater such
25 as a ceramic resistive heating plate, providing growth
26 temperatures as high as, for example, but not by way of
27 limitation 450 °C. The temperature can be controlled
28 by changing current to the heater, which can be
29 initially calibrated against a thermocouple attached to
30 the sample.

1 A solid TaCl_5 (powder) source contained in a glass tube
2 can be used as the metal precursor. Although TaCl_5 may
3 be used as the halide precursor for Ta, other Ta
4 halides including TaF_5 , TaI_5 , and TaBr_5 may also be
5 used. The glass tube can be maintained at 100°C to
6 develop adequate vapor pressure. All the delivery lines
7 are preferably heated to between 130°C and 150°C to
8 prohibit condensation of the precursor. To improve the
9 delivery, argon can be used as a carrier gas, with the
10 flow being controlled by, for example, a leak valve
11 upstream from the tube containing the source.

12
13 Atomic hydrogen and activated nitrogen may be generated
14 by a quartz tube connected to the sample chamber via,
15 for example, a gate valve. Hydrogen and nitrogen gases
16 may be supplied via, for example, a leak valve. The
17 quartz tube may be wrapped with a multiple-turn coil
18 carrying radio frequency energy at 13.56 MHz, with a
19 power level of, for example, up to 1200 watts.
20 Preferably, the gate valve is used between the sample
21 chamber and the tube region so that the precursor is
22 not exposed to the tube region. Optical emission
23 spectroscopy may be used to monitor the generated
24 radicals. Large atomic H peaks are observed for H
25 plasma, while only N_2^+ related peaks for N plasma,
26 indicating that the active precursor for N is activated
27 molecular nitrogen rather than atomic N. This
28 difference between H and N may be due to the higher
29 dissociation energy of molecular nitrogen.

30

1 The deposition cycle comprises the following steps:
2 exposing the substrate to TaCl_5 carried by Ar gas,
3 evacuating the chamber, opening the hydrogen and
4 nitrogen source valves and initiating the RF plasma for
5 a set time, and shutting off the hydrogen and nitrogen
6 source and plasma, allowing the chamber to return to
7 base pressure. Before the cycle begins, the partial
8 pressure of hydrogen and nitrogen were set using leak
9 valves. This cycle ideally results in the complete
10 reaction of the adsorbed TaCl_5 layer, and the
11 deposition of a fraction of a monolayer of TaN. For Ta
12 PE-ALD, the same process is used, with no nitrogen and
13 the nitrogen valve closed.

14
15 While silicon or silicon dioxide substrates are used
16 for deposition, poly-silicon substrates are used for
17 copper diffusion barrier property measurement. However,
18 the invention is not limited to the use of silicon or
19 silicon dioxide substrates. Deposition may be performed
20 on various substrates, such as metals including Cu, Ta,
21 TaN, Ru, W and dielectrics such as SiCO, MSQ (methyl
22 silsesquioxane), HSQ (hydrogen silsesquioxane) based
23 low k, or high k oxides including HfO_2 , ZrO_2 . For this
24 purpose, an ultra-high vacuum (UHV) direct current (DC)
25 magnetron sputtering chamber connected through a load
26 lock chamber may be used for the deposition of
27 sputtered copper films on the ALD films without
28 breaking vacuum. An in-situ resistivity and optical
29 scattering measurement system may be used for diffusion
30 barrier temperature determination. Annealing can be

performed at, for example, 3 °C/s up to 1000 °C in a helium environment.

Example

Tantalum nitride films are grown typically with TaCl₅ exposure time of 2 seconds and plasma exposure time of 5 seconds, which correspond to saturation condition of ALD. This saturation is due to the self-limited adsorption of the precursor. The total time for one cycle is typically 12 seconds including the evacuation time after TaCl₅ and plasma exposures. The hydrogen partial pressure during exposure is set as 2.5×10^{-3} Torr and nitrogen partial pressure is changed. The total pressure (argon and TaCl₅ vapor) during TaCl₅ exposure is constant at 3.0×10^{-2} Torr. A typical number of cycles is 50 - 800 to produce tantalum nitride films with thicknesses in the range of 20 to 400 Angstroms, depending upon growth conditions.

Fig. 1 illustrates X-ray diffraction (XRD) results of PE-ALD TaN_x grown at T_s = 300°C. At low nitrogen partial pressure (nitrogen to hydrogen partial pressure ratio = 0.001), the XRD spectrum shows a broad peak at approximately $2\theta = 38^\circ$. For a higher partial pressure ratio (0.004), the broad peak shifts to a lower 2θ value, indicating the formation of other phases. The hump in the diffraction peak at approximately 34°C can be indexed as Ta₂N (100) ($2\theta = 33.968^\circ$) or hexagonal TaN (110) (curve b, $2\theta = 34.528^\circ$). It is difficult to

1 discern the difference due to the large width of the
2 peak.

3
4 With further increasing nitrogen partial pressure above
5 a partial pressure ratio of 0.025, well-distinguished
6 cubic TaN peaks are observed (111 peak at $2\theta = 35.876^\circ$
7 and 200 peak at $2\theta = 41.638^\circ$). This indicates that the
8 PE-ALD TaN films are composed of polycrystalline grains
9 in contrast to PE-ALD Ta films grown at similar
10 temperature. High resolution transmission electron
11 microscope (TEM) observation also show well defined
12 lattice fringes for the TaN films. Diffraction peaks of
13 other phases such as hexagonal TaN, Ta_5N_6 , or Ta_3N_5 were
14 not observed for partial pressure ratio up to $P_{N_2}/P_{H_2} =$
15 0.25. Above $P_{N_2}/P_{H_2} = 0.5$ additional features begin to
16 appear at approximately $2\theta = 35^\circ$, which can be indexed
17 as a higher N content phase such as Ta_3N_5 (004 or 040
18 peak at $2\theta = 34.939^\circ$) or Ta_5N_6 (040 or 110 peak at $2\theta =$
19 34.629°).

20
21 In Fig. 2, the nitrogen content of the TaN films was
22 determined by Rutherford Backscattering Spectrometry
23 (RBS). The results are shown as a function of partial
24 pressure ratio between nitrogen and hydrogen (P_{N_2}/P_{H_2})
25 for the films grown at $T_s = 300^\circ\text{C}$. With increasing
26 P_{N_2}/P_{H_2} from 0.001 to 1, the N/Ta ratio of grown TaN
27 films was changed from 0.3 to 1.4. These results
28 together with XRD analysis mentioned above indicate
29 that the cubic TaN films are grown at the partial
30 pressure ratio between 0.7 and 1.3. Stoichiometric TaN

1 was obtained at $P_{N_2}/P_{H_2} = 0.025-0.035$. The stoichiometry
2 of TaN can be controlled since atomic H extracts the Cl
3 atoms while the N is incorporated from activated
4 nitrogen. This ability to change the stoichiometry has
5 potential benefits for PE-ALD of TaN. With increasing
6 P_{N_2}/P_{H_2} from 0 to 1, the N/Ta ratio of grown TaN films
7 is changed from 0 (Ta) to 1.7.

8
9 The number of Ta atoms incorporated during one cycle
10 obtained by RBS, corresponding to the growth rate, is
11 also plotted as a function of partial pressure ratio
12 P_{N_2}/P_{H_2} in Fig. 2. Fig. 2 shows that the growth rate
13 increases continuously, and linearly, with increasing
14 nitrogen partial pressure. The number of tantalum
15 atoms deposited per cycle at the stoichiometric
16 composition was $1.0 \times 10^{14}/\text{cm}^2$.

17
18 Referring to Fig. 3, resistivity of the grown TaN is
19 typically $350-400 \mu\Omega\text{cm}$ for cubic TaN and overall,
20 resistivity tends to increase with increasing nitrogen
21 concentration. For example, the TaN film grown at
22 $P_{N_2}/P_{H_2} = 0.65$ has resistivity of $7200 \mu\Omega\text{cm}$. The high
23 resistivity may be explained by the formation of a high
24 resistivity Ta_3N_5 phase.

25
26 Fig. 4 shows the growth rates and N/Ta ratio of TaN
27 films as a function of plasma exposure time t_p . The
28 growth rate increases with increasing plasma exposure
29 until $t_p = 2$ seconds then decreases somewhat to
30 saturate above $t_p > 4$ seconds. The growth rates as a

1 function of TaCl_5 exposure time T_{TaCl} (data not shown)
2 saturate at $T_{\text{TaCl}} > 1$ second without showing any maximum
3 below saturation. The number of Ta atoms deposited per
4 cycle at saturation condition was $1.2 \times 10^{14}/\text{cm}^2$. In
5 addition, the N/Ta ratio in the films tends to increase
6 with t_p .

7
8 RBS and FRES (Forward Recoil Elastic Spectrometry)
9 results for the TaN films are shown as a function of t_p
10 in Fig. 5. The Cl content is a strong function of t_p ,
11 and the resistivity values, shown together, indicate
12 that the growth of films with low Cl and resistivity
13 requires $t_p > 5$ seconds. Hydrogen concentration in the
14 films increases with t_p , but saturates above 5 seconds.
15 The maximum hydrogen concentration was approximately
16 11%.

17
18 The oxygen content for the films grown at saturation
19 condition was typically between 5-10 %, independent of
20 growth temperatures. However, the oxygen content shows
21 a tendency to increase with decreasing film thickness.
22 In addition, the sheet resistance values of very thin
23 films (especially below 100 Å) increase by up to 5 - 10
24 % after exposure to the air. These results imply that
25 the oxygen is incorporated by air exposure rather than
26 during growth. For TaN films capped with copper without
27 an air break, detailed analysis by RBS shows that the
28 oxygen content is below detection limit (5 %) inside
29 the films. Oxygen was only detected at the interface
30 region, supporting that the oxygen is incorporated by

1 air exposure. No carbon was detected by RBS, within a
2 detection limit of 5 at %.

3
4 The effect of growth temperature during PE-ALD TaN is
5 studied in the range of $T_s = 100 - 400$ °C. The XRD
6 spectra of the TaN films grown at different
7 temperatures are shown in Fig. 6. All spectra show only
8 cubic TaN related peaks, although the intensity ratio
9 between 111 and 200 peaks depends on growth
10 temperature. At even the lowest growth temperature of
11 100 °C, the 111 peak is clearly seen.

12
13 Fig. 7 shows that the N/Ta ratio of the film is almost
14 independent of growth temperature, while the growth
15 rate is strong function of growth temperature. With
16 increasing growth temperature from 100 to 400 °C, the
17 growth rate increases by almost a factor of three then
18 saturates above $T_s = 300$ °C.

19
20 Fig. 8 shows the chlorine and hydrogen content and
21 resistivity of TaN films as a function of growth
22 temperature. Both chlorine and hydrogen contents
23 decrease with increasing growth temperature. At typical
24 growth condition (300 °C), chlorine content is below
25 0.5 % and hydrogen content is below 10 %. Although the
26 dependence is weaker, the resistivity also decreases
27 with growth temperature. This decrease in resistivity
28 is probably due to the smaller chlorine content for
29 higher growth temperatures.

1 The discussion above indicates, in summary, that TaN_x
2 ($x = 0$ to 1.7) films with various nitrogen content are
3 easily deposited by the present invention. However, in
4 accordance with the invention, a TaN/Ta bilayer is
5 deposited by growing a Ta PE-ALD film on PE-ALD of TaN
6 for desired thickness, such as 25 \AA . This may be done
7 by simply switching off the nitrogen valve during
8 deposition. For comparison, PE-ALD Ta and TaN films of
9 the same thickness were grown. After a copper PVD
10 capping layer deposition without air exposure,
11 resistivity and optical scattering measurements are
12 performed during annealing for copper diffusion barrier
13 property measurement.

14
15 Fig. 9 shows that the bilayer structure has better
16 diffusion barrier failure temperature than the
17 individual layers. This is partly because the Ta
18 PE-ALD layer has an amorphous structure which
19 contributes to the copper diffusion barrier properties
20 by reducing the number of grain boundaries (Grain
21 boundaries are the predominant copper diffusion
22 mechanism). Further, the inherently better copper
23 diffusion barrier property of the TaN , as opposed to
24 that of a Ta single layer, positively contributes to
25 the resulting diffusion barrier properties. In summary,
26 both the amorphous PE-ALD tantalum layer and PE-ALD
27 tantalum nitride layer positively contribute to the
28 resulting diffusion barrier properties.

29

1 The bilayer structure concept can be extended to the
2 deposition of multi-layer structures composed of Ta and
3 TaN. The nitrogen flow can be easily turned on and off.
4 Thus by using simple computer control, a multi-layer
5 structure with a desirable thickness for each layer can
6 be deposited easily. This multi-layer structure can be
7 used as a diffusion barrier, or for other semiconductor
8 related processes. In addition, by changing the number
9 of cycles of each Ta and TaN layer process, the overall
10 control of nitrogen content can be more precisely
11 defined.

12
13 It is noted that the foregoing has outlined some of the
14 more pertinent objects and embodiments of the present
15 invention. The concepts of this invention may be used
16 for many applications. Thus, although the description
17 is made for particular arrangements and methods, the
18 intent and concept of the invention is suitable and
19 applicable to other arrangements and applications. It
20 will be clear to those skilled in the art that other
21 modifications to the disclosed embodiments can be
22 effected without departing from the spirit and scope of
23 the invention. The described embodiments ought to be
24 construed to be merely illustrative of some of the more
25 prominent features and applications of the invention.
26 Other beneficial results can be realized by applying
27 the disclosed invention in a different manner or
28 modifying the invention in ways known to those familiar
29 with the art. Thus, it should be understood that the
30 embodiments has been provided as an example and not as

1 a limitation. The scope of the invention is defined by
2 the appended claims.
3